

**REMARKS**

Claim 1 has been amended. Claims 1-29 are pending in the application.

**Withdrawal of Prior Rejection Under 35 U.S.C. 103(a)**

Applicants respectfully acknowledge withdrawal of the final rejection of claims 1-29 under 35 U.S.C. 103(a) based on the disclosure in U.S. Patent No. 2,027,182 to Lazier.

Applicants note that on page 2 of the Office action, the Examiner asserts that claim 1 as amended requires that the portion of liquefiable products of the intermediate reaction product mixture subjected to selective hydrogenation in step (c) be "comprised predominantly of ethyl acetate." However, such a limitation regarding the composition of the liquefiable products of the intermediate reaction product mixture is not specified in claim 1, nor is it required to distinguish the disclosure in Lazier. In any event, the liquefiable products of the intermediate reaction product mixture does not have to be comprised predominantly of ethyl acetate. As disclosed, for example, in Table 1 on page 25 of the specification, the composition of the material in line 37 fed to the hydrogenation reactor 38 is predominantly ethanol (69.67 mol %), not ethyl acetate (21.18 mol %).

**Double Patenting Rejection**

In response to the rejection of claims 1-29 under the judicially created doctrine of obviousness-type double patenting as being unpatentable over claim 1, 2 and 11-23 of U.S. Patent No. 6,632,330, applicants submit a Terminal Disclaimer in accordance with 37 CFR 1.130(b) and 37 CFR 1.321(c) disclaiming the amount of any term of a patent issuing from the present application that extends beyond the term of U.S. Patent No. 6,632,330. The subject application and U.S. Patent No. 6,632,330

are commonly assigned to Davy Process Technology Limited (formerly Kvaerner Process Technology Limited). Applicants respectfully submit that filing of the terminal disclaimer is not an admission as to the merits of the rejection.

**Claims 28 and 29**

The double patenting rejection notwithstanding, applicants note that the invention defined in dependent claims 28 and 29 is not subject to any other rejection and are submitted as defining patentable subject matter.

**Rejection under 35 U.S.C. §103(a)**

Reconsideration is respectfully requested of the rejection of claims 1-9 and 11-27 under 35 U.S.C. §103(a) based on the disclosure of U.S. Patent No. 2,524,899 to Dunn (Dunn) alone or in view of U.S. Patent No. 1,708,460 to Zeisberg (Zeisberg) and the rejection of claim 10 under 35 U.S.C. §103(a) based on the disclosure in Dunn in view of "Heterogeneous Catalysts", Johnson Matthey Chemicals, 1981-1984, page 6 (Johnson Matthey). The invention defined in claims 1-27 is submitted as patentable over the disclosures in the cited references.

Independent claim 1 is directed to a process for the preparation of ethyl acetate. Claim 1 as amended requires:

- (a) converting a C<sub>2</sub> feedstock comprising ethanol to ethyl acetate in an ethyl acetate production zone by a procedure selected from:
  - (i) dehydrogenation, and
  - (ii) reaction with acetaldehyde
- (b) recovering from the ethyl acetate production zone an intermediate reaction product mixture comprising hydrogen and liquefiable products comprising the majority of the ethyl acetate produced in step (a), ethanol, and by-products containing reactive carbonyl groups;

- (c) passing at least a portion of the liquefiable products of the intermediate reaction product mixture as recovered from the ethyl acetate production zone to a selective hydrogenation zone and contacting the liquefiable products of the intermediate reaction product mixture with a selective hydrogenation catalyst in the presence of hydrogen in the selective hydrogenation zone maintained under selective hydrogenation conditions effective to selectively hydrogenate said by-products containing reactive carbonyl groups to corresponding alcohols;
- (d) recovering from the selective hydrogenation zone a selectively hydrogenated reaction product mixture comprising ethyl acetate, ethanol, hydrogen and hydrogenated by-products comprising said corresponding alcohols;
- (e) distilling the selectively hydrogenated reaction product mixture in one or more distillation zones so as to produce a first composition comprising substantially pure ethyl acetate and a second composition comprising ethanol and water;
- (f) treating the second composition of step (e) to separate water therefrom and yield a third composition comprising ethanol with a reduced water content; and
- (g) recovering the third composition of step (f).

As amended, the process of claim 1 now more clearly requires that the liquefiable products introduced into the selective hydrogenation zone and contacted with the selective hydrogenation catalyst be a portion of the intermediate reaction product mixture as recovered from the ethyl acetate production zone. Support for the amendment to claim 1 may be found, for example, at page 12, lines 20-30; page 21, line 24 to page 22, line 28 and Fig. 1.

In order to establish a *prima facie* case of obviousness, the reference, or references when combined, must teach or suggest all of the claim limitations. The Patent Office must also establish

that there is some suggestion or motivation to combine the reference teachings.

Zeisberg describes a process for manufacturing various esters and other organic compounds including the preparation of ethyl acetate from ethyl alcohol. In accordance with the process of Zeisberg, ethyl alcohol may be converted to ethyl acetate by contacting the alcohol with a dehydrogenation catalyst under pressure. As acknowledged on page 6 of the Office action, Zeisberg fails to disclose any method for purifying the ethyl acetate product, much less the process as defined in steps (c) through (f) of claim 1. Applicants respectfully submit that the shortcomings of Zeisberg cannot be overcome by resort to Dunn.

Dunn describes a process of purifying alkyl esters of lower fatty acids containing hydrocarbon and aldehyde impurities. In accordance with the process of Dunn, ethyl acetate of high purity is obtained from relatively crude mixtures of ethyl acetate containing from about 50% to about 55% ethyl acetate. These relatively crude mixtures are described as the liquid residue from the reaction of acetaldehyde and ethanol in processes for producing butadiene. However, in the purification scheme of Dunn, this residue is first distilled with a lower aliphatic saturated alcohol (e.g., methanol) in an amount sufficient to remove all of the hydrocarbons present as low boiling azeotropes to produce a residue containing little or no hydrocarbons.<sup>1</sup> This partially purified residue substantially free of hydrocarbons may then be subjected to vapor phase or liquid phase hydrogenation in the presence of a hydrogenation catalyst to reduce aldehydes and ketones present in the residue to the corresponding alcohols. The reaction mixture from the hydrogenation is then fractionally

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<sup>1</sup> Contrary to the assertion on page 7 of the Office action, the close boiling impurities said to be removed by azeotropic distillation with a lower aliphatic saturated alcohol in Dunn are the hydrocarbons listed at the top column 2, not aldehydes or ketones.

distilled to produce an ethyl acetate having a purity of 97% or greater.

Accordingly, in contrast to the claimed invention, Dunn fails to disclose or suggest a purification scheme in which liquefiable products as recovered from the ethyl acetate production zone are introduced into a selective hydrogenation zone. It will be noted that the disclosure in Dunn relates to the treatment of a stream by selective hydrogenation that has already undergone some degree of purification. Thus, it is a very different stream as compared to the portion of the liquefiable products of the intermediate reaction product mixture stream of claim 1 that is recovered from the reaction for the production of ethyl acetate from ethanol and contacted with a selective hydrogenation catalyst.

With reference to Example 1 of Dunn it will be noted that the starting material of the example is a crude by-product oily mixture. As indicated in the description of Dunn, this oily mixture is purified by first carrying out a preliminary clean-up by azeotropic distillation with methanol on a product stream that has itself already been the subject of a separation step. It can be noted that the initial oily mixture of Example 1 of Dunn contains only 2.6% ethanol and only 0.7% water (i.e., trace amounts). This oily mixture is subjected to azeotropic distillation with methanol in which substantially all of the ethanol and water as well as hydrocarbons would be removed. It is the product of this separation and treatment that is then subjected to the hydrogenation step. It will therefore be appreciated that the material that is being treated in the hydrogenation step of Dunn is not a portion of the "impure" liquefiable product as recovered from the ethyl acetate production zone as called for in claim 1. The hydrogenation step as described in Dunn is simply a final polishing step on a feed that already contains low levels of impurities.

The Examiner will note that although good levels of purity are noted in Example 1 of Dunn including, for example, the combined aldehyde and ketonic component that applicants deduce is butyraldehyde and methylethylketone present in the crude oily mixture and which are close boiling to the desired product is reduced in the polishing step from about 17.3% to 0.7%, there is no disclosure that the process could be operated with an "impure" stream such as a portion of the liquefiable products of the intermediate reaction product mixture recovered from the ethyl acetate production zone as called for in claim 1. Instead, one of ordinary skill in the art is taught that the concentration of hydrocarbons and other impurities, alkanol and water must be reduced down to trace levels before the hydrogenation step is conducted. Thus, Applicants respectfully submit the disclosure in Dunn teaches away from the process of the present invention.

In addition, applicants direct the Examiner's attention to column 2, lines 37-42 of Dunn where it is noted that the process is restricted to that in which "just sufficient alcohol is employed to ensure the approximately complete removal of the hydrocarbons in the form of hydrocarbon-alcohol azeotropes, thereby avoiding a needless distillation of the ester to remove the last of the alcohol". It is further noted that Fig. 1 of Dunn illustrating a continuous apparatus for performing the disclosed process shows excess alcohol-ester azeotrope, 45, being removed from the residue prior to hydrogenation. Further, the product of hydrogenation, 53, is distilled to produce an overhead ethyl acetate product fraction and a heavy residues stream without further separation of alcohol. In addition it is noted that the description of Dunn (for example, column 3, lines 5-24) describes removing overhead residual alcohol before hydrogenating the residue from the distillation. Consequently, Dunn teaches that the feed to the hydrogenation reactor needs to be substantially alcohol free if the product is to meet the required specification.

It is therefore apparent that the entire disclosure and teaching of Dunn is to hydrogenate a stream of ethyl acetate that has been first treated by azeotropic distillation to substantially remove alcohol, hydrocarbons and other impurities.

It is acknowledged that in the example of Dunn, as a result of an inadequate separation prior to hydrogenation, some alcohol was present in the material hydrogenated and was thus subsequently separated. However, this does not bring Dunn within the scope of claim 1, nor does Dunn render Claim 1 obvious over the disclosure therein. This is because Claim 1 requires that the hydrogenation of step (c) be carried out on at least a portion of the liquefiable products of the intermediate reaction product comprising ethyl acetate, ethanol and by-products. The present invention as defined by claim 1 seeks to avoid the problem of separating close boiling ketone and aldehyde impurities from ethyl acetate by distillation, the consequence of this requirement is that the selective hydrogenation of step (c) must reduce the impurities containing reactive carbonyl groups to concentration levels which result in a "substantially pure" ethyl acetate product. It will be accepted that a "substantially pure" product is one that is suitable for use without further purification.

The Examiner will be interested to learn that the maximum methylethylketone concentration currently allowable in commercial ethyl acetate products is about 100 to 50 ppm. In this connection reference may be made to page 1, line 19 of WO 03/011809, a copy of which is enclosed. It is acknowledged that this application was published after the priority date of the present application. However, it is simply being referred to show the purity levels accepted commercially for ethyl acetate and thus applicants believe referring to it is appropriate.

It is therefore apparent that the ethyl acetate purity of 97 to 99% achieved in Dunn (see column 3, line 61 to 64) would no longer meet commercial product specifications. In addition, the

methylethylketone concentrations achieved of 1000 to 3000 ppm (by weight) are an order of magnitude higher than those required to meet current commercial specifications.

Thus, not only does Dunn not subject an liquefiable products of an intermediate reaction product mixture as recovered from an ethyl acetate production zone to hydrogenation as required by claim 1, it does not produce a substantially pure product as would be understood by one of ordinary skill in the art at the priority date of the present application which will be acknowledged is some 50 years after the publication of Dunn.

The Examiner has suggested that it would be obvious to combine the teaching in Dunn with that in Zeisberg. However, as noted by the Examiner Zeisberg does not disclose any particular method of purifying the ethyl acetate produced by the process. He therefore suggests that the person of ordinary skill in the art would look to the teachings of Dunn. However, as noted above, Dunn teaches the need to carry out substantial purification of the ethyl acetate by conventional means including azeotropic distillation with an alcohol prior to carrying out any selective hydrogenation. In any event, following Dunn would not achieve a level of purity in the ethyl acetate product suitable to meet today's commercial requirements. Thus, even if the skilled person would combine the teachings of Dunn and Zeisberg which have both been available for in excess of 50 years, the combination would not be lead to the process of the present invention.

In view of the above, applicants respectfully submit the Office has failed to establish a *prima facie* case of obviousness with respect to claim 1 based on the disclosure of Zeisberg and Dunn. Applicants submit claims 2-9 and 11-27, which depend directly or indirectly from claim 1, are likewise patentable over the cited references for the reasons set forth above regarding claim 1 and the additional limitations incorporated therein. Furthermore, the shortcomings in the teachings of Zeisberg and/or



Dunn with respect to claim 1 cannot be overcome by resort to the disclosure in "Heterogeneous Catalysts", Johnson Matthey Chemicals, 1981-1984, page 6 (Johnson Matthey). Accordingly, dependent claim 10 which depends indirectly from claim 1 is likewise submitted as patentable over the cited references.

**Information Disclosure Statement**

Applicants acknowledge the Examiner's consideration of items 13, 14, 18, and 21 listed on the Supplemental Information Disclosure Statement submitted October 21, 2002 to the extent they are characterized in the specification.

**Conclusion**

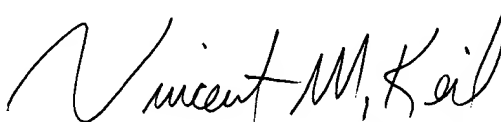
In view of the above, favorable reconsideration and allowance of all pending claims are respectfully solicited.

Applicants request an extension of time to and including May 14, 2004 for filing a response to the above-mentioned Office action.

A check in payment of the applicable extension  
\* fee and terminal disclaimer fee under 37 CFR 1.20(d) is enclosed.

The Commissioner is requested to charge any fee deficiency in connection with this amendment to Deposit Account No. 19-1345.

Respectfully submitted,



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(54) Title: PROCESS FOR SEPARATING SEC-BUTANOL FROM ETHYL ACETATE

(57) Abstract: A process for separating secondary-butanol impurity from ethyl acetate (EtAc) by feeding the impure EtAc to a distillation column operating at a pressure of less than 1 bar absolute to provide (1) a stream comprising EtAc as a major component and (2) a residue or a second stream comprising at least some sec-butanol from said impure EtAc. The process can be applied to purifying EtAc derived from (a) catalytic reaction of ethylene with acetic acid followed by (b) a hydrogenation step. The 2-butanone impurity produced in step (a) is difficult to separate from EtAc, and step (b) converts it to sec-butanol which can be separated by the reduced pressure fractionation of the invention.

WO 03/011809 A1

## PROCESS FOR SEPARATING SEC-BUTANOL FROM ETHYL ACETATE

This invention relates to process for removing a sec-butanol impurity from a product stream comprising ethyl acetate.

Ethyl acetate may be produced by several methods known in the art. One such method comprises reacting ethylene with acetic acid in the presence of an acidic catalyst, for example, an acidic heteropolyacid catalyst. In a second such method, ethyl acetate is produced by converting an alcohol feedstock by i) dehydrogenation, ii) oxidation, iii) reaction with an aldehyde or iv) oxidation to the corresponding aldehyde followed by the Tischenko reaction (see, for example, EP 0992484).

These reactions can produce a product stream comprising ethyl acetate, unreacted starting materials, a number of aldehyde and ketone impurities, such as acetaldehyde, methyl i-propyl ketone, butyraldehyde, methyl propyl ketone, methyl i-butyl ketone, methyl - s-butyl ketone, methyl i-pentyl ketone, methyl ethyl ketone (MEK), as well as variety of C8, branched and higher alkenes, such as methyl heptene and dimethyl hexene. The unreacted starting materials are recovered from the product stream, and recycled to the reactor. The ethyl acetate may be recovered from the remainder of the product stream, for example, by distillation. Unfortunately, some aldehyde and/or ketone impurities, such as MEK, have a boiling point that is very similar to the boiling point of ethyl acetate and, for example, it is difficult to reduce or maintain the MEK concentrations of the final product to below 50 ppm using this method.

Various attempts have been made to reduce the concentration of such aldehyde and/or ketone impurities in alkyl alkanoate streams further. As aldehydes and ketones may form azeotropes with alkyl alkanoates, attempts have been made to separate the

impurities using azeotropic distillation (see for example EP 0151886).

EP 0992484 describes a process in which aldehyde and/or ketone impurities are removed from an alkyl alkanoate product stream by contacting the impure alkyl alkanoate product stream with a selective hydrogenation catalyst of, for example, ruthenium in the presence of hydrogen. The hydrogenation reaction is preferably carried out at elevated pressures of 25 to 50 barg. Under the reaction conditions, the aldehyde and/or ketone impurities are selectively hydrogenated to the corresponding alcohols, leaving the alkyl alkanoate substantially unreacted. As many alcohols tend to boil at a very different temperature to alkyl alkanoates, the former can be separated by simple distillation.

However, it has been found that in the case of ethyl acetate and MEK, the alcohol formed by hydrogenation of MEK, sec-butanol, is harder to separate from the desired ethyl acetate, because the ethyl acetate and sec-butanol form a pinch under conventional distillation conditions at atmospheric pressure. A column is said to be pinched when the component balance line is too close to the equilibrium curve. The practical significance is that very little separation is taking place and the use of many separation stages may only result in a very small change in composition. Hence it becomes very difficult to reduce the sec-butanol in the ethyl acetate to a low level. A pinch can be remedied by increasing the reflux and reboil, thus drawing the component balance line and the equilibrium curve further apart, but this is achieved at a penalty of significantly greater energy consumption.

We have now found that the pinch can also be eased, and the sec-butanol level in ethyl acetate can be reduced further, i.e. ethyl acetate of higher purity can be obtained, by the use of reduced pressure in the corresponding distillation column.

Accordingly, the present invention provides a process for separating ethyl acetate from sec-butanol, said process comprising:

- taking a product stream comprising ethyl acetate and sec-butanol,
- feeding the product stream to a distillation column,
- operating the distillation column at a pressure of less than 1 bar absolute to give an ethyl acetate stream and a sec-butanol stream.

Thus one aspect of the present invention provides a process for separating sec butanol impurity from ethyl acetate, said process comprising:

feeding to a distillation column a product stream comprising at least ethyl acetate and sec-butanol,

operating the distillation column at a pressure of less than 1 bar absolute to provide at least

- 5 (1) a stream comprising ethyl acetate as a major component and  
(2) a residue or a second stream which residue or second stream comprises at least some sec-butanol from said product stream

Under the reduced pressure conditions of the present invention it has been found that the ethyl acetate / sec-butanol pinch can be eased and improved separation can be  
10 obtained. Ethyl acetate product is thus removed as an overhead stream.

Preferably the distillation column of the present invention is operated so that the pressure in the column lies in the range 0.01 and 0.95 bar absolute, more preferably between 0.1 and 0.7 bar absolute, and most preferably between 0.3 and 0.5 bar absolute.

The feed to the distillation column will preferably be introduced between one-  
15 quarter and three-quarters of the way up the column, more preferably in the central third. Most preferably the feed will be between one-third and halfway up the column from the base. It will be readily apparent to one skilled in the art that the exact operating conditions of the column may depend on a number of factors, for example, the number of stages, the purity of the feed and the purity of product desired. For example, in a  
20 distillation column with 25 theoretical stages, the feed to the column is preferably located 15 stages below the top of the column. Preferably the column is operated at a reflux ratio of 2:1. Under these conditions and at a pressure of 0.5 bara, then the temperature at the head of the column, containing largely EtAc, would be 57.3 deg C.

The level of sec-butanol in the final EtAc product may be further reduced by  
25 control of the base purge of the distillation column. In general an increased purge rate will lead to a reduction in the base level of sec-butanol and hence a reduced level in the heads, but at the expense of loss of other products in the purge.

It has now been found that under the conditions of operation of the distillation column that there is a second effect of varying the purge rate which favours reduced  
30 purge rates. It has been found that sec-butanol may react in the base of the column with either acetic acid (which is produced in the column by hydrolysis of the EtAc) or directly with EtAc. Both of these reactions lead to production of sec-butylacetate, with

by-products of water and ethanol respectively. The sec-butylacetate formed may be easily separated from the EtAc by the column of the current invention. With reduced purge rates any sec-butanol in the base will have an increased residence time and hence the extent of reaction will be increased.

5       Hence there are two competing processes determining the level of sec-butanol in the base of the column. Reduction of the base level of sec-butanol can be achieved directly by increased purge rate. However reduction of the base level of sec-butanol can also be achieved by increased reaction of the sec-butanol. Due to the competing process of sec-butanol reaction, the purge rate required in the distillation may be expected to be  
10       less than that required in the absence of the competing process.

Preferably, purge rates are adjusted throughout the life of a catalyst. For example, initial purge rates may be low as a fresh catalyst may produce less MEK, but as the catalyst ages it may produce increased MEK (and hence sec-butanol) and purge rates may be increased.

15       It will also be apparent that the rate of reaction of sec-butanol with acetic acid will depend on the amount of acetic acid in the base of the column. It is therefore possible to control the rate of reaction of the sec-butanol with acetic acid by changing the amount of acetic acid in the base of the column. For example, increased reaction rates can be obtained by addition of further acetic acid directly in the base of the column or to the  
20       EtAc / sec-butanol stream prior to the column. This will also affect the purge rate required in the distillation column.

It will be readily apparent to one skilled in the art that the process of the present invention using distillation under reduced pressure is readily applicable to separation of an ethyl acetate / sec-butanol stream derived from any source.

25       In a preferred embodiment of the present invention the ethyl acetate / sec-butanol stream is derived from a stream comprising ethyl acetate and methyl ethyl ketone (MEK), wherein the MEK has been hydrogenated to produce the sec-butanol.

In a further preferred embodiment the ethyl acetate / MEK stream has itself been derived from the reaction of ethylene and acetic acid, or from the conversion of an  
30       alcohol feedstock to ethyl acetate by i) dehydrogenation, ii) oxidation, iii) reaction with an aldehyde or iv) oxidation to the corresponding aldehyde followed by the Tischenko reaction.

For example, the reaction conditions necessary for producing ethyl acetate from the reaction between ethylene and acetic acid are well-known in the art, and are described by way of example in GB-A-1259390. As well as ethyl acetate, the product stream comprises aldehyde and/or ketone impurities. Examples of aldehyde impurities include acetaldehyde, propionaldehyde, butyraldehyde, valeraldehyde. Examples of ketone impurities include methyl iso-propyl ketone, methyl propyl ketone, methyl iso-butyl ketone, methyl-sec-butyl ketone, methyl-iso-pentyl ketone and MEK (methyl ethyl ketone). These impurities may form more than 5 ppm, preferably, 5 to 1000 ppm, more preferably, 5 to 500 ppm of the product stream, prior to treatment.

The MEK in this product stream is hydrogenated to produce sec-butanol, for example, by contacting all or a part of the product stream comprising MEK with hydrogen in the presence of a selective hydrogenation catalyst. Other impurities that comprise the product stream may also be selectively hydrogenated. The selective hydrogenation catalyst is selected to be relatively active with respect to the hydrogenation of aldehyde and/or ketone carbonyl groups, but relatively inactive with respect to the hydrogenation of alkyl alkanoate carbonyl groups. Suitable catalysts comprise transition metals such as nickel, palladium, platinum, ruthenium, rhodium and rhenium. Such catalysts may be supported, for example, on alumina, silica or carbon. The metal loadings on such supported catalysts may range from 0.1 to 50 wt %, preferably, 0.5 to 10 wt %. Examples of specific catalysts include Ni on alumina or silica, Ru on carbon or silica, Pd on carbon, Rh on carbon and Pt on carbon. In a preferred embodiment, a 3-5wt% Ru catalyst supported on carbon or silica is employed.

The selective hydrogenation step may be carried out in the presence of any suitable solvent, for example, water, and/or alkyl alkanoate.

The hydrogen employed in the selective hydrogenation step may be employed in pure or impure form. Optionally, an inert gas such as nitrogen may be co-fed to the reaction.

The selective hydrogenation step may be carried out at 40 to 120°C, preferably, 80-100°C. The combined partial pressure of the product stream and hydrogen employed in the hydrogenation step may range from 1 to 80 barg (bar gauge), preferably, 1 to 50 barg, more preferably, 1 to 40 barg.

The mole ratio of the product stream to hydrogen employed may be 1000:1 to 5:1,

preferably from 100:1 to 10:1, for example, 60:1.

The product stream may be passed over the selective hydrogenation catalyst at a liquid hourly space velocity (LHSV) of  $0.1 \text{ hr}^{-1}$  to  $20 \text{ hr}^{-1}$ , preferably,  $1 \text{ hr}^{-1}$  to  $15 \text{ hr}^{-1}$ , and most preferably 5 to  $10 \text{ hr}^{-1}$ .

5 Under the selective hydrogenation conditions used in the preferred process of the present invention, the MEK impurity is selectively hydrogenated to sec-butanol. Any other aldehyde and/or ketone impurities are also hydrogenated to their corresponding alcohols. The hydrogenated stream so produced comprises ethyl acetate and sec-butanol. In certain embodiments this stream may be further treated prior to feeding to  
10 the distillation column operating at a pressure of less than 1 bar absolute as described previously. Preferably the stream may be treated to remove any unreacted hydrogen. Hydrogen separation may be achieved, for example, by using a flash tank or a separation column. The separated hydrogen may be purged or recycled for re-use. In another  
15 embodiment the stream may undergo further separation stages prior to the separation of the ethyl acetate and sec-butanol, to remove other components, such as, for example, water, ethanol and other alcohols formed in the hydrogenation reaction. Aqueous phases may be removed, for example, using a settling unit. Most preferably the hydrogenated stream may be mixed with water and then fed to a decanter. The aqueous  
20 phase comprising a major proportion of ethyl acetate may also be fed to a distillation column for further separations prior to the stream comprising ethyl acetate and sec-butanol being fed to the distillation column at reduced pressure of the present invention.

#### Example 1

Experiments were run on a 50-tray pilot plant distillation column to test the efficiency  
25 for removing s-BuOH from the final product. Small samples could be taken at intervals from both the reboiler sump at the base of the column and the reflux drum at the top, and from above various intermediate trays within the distillation column. The column reboiler was charged with the mixture in table 1 below:

30



Component	m/m %
Ethyl acetate	62
Ethyl propionate	10
s-Butyl acetate	3
s-BuOH	9
Misc. hydrocarbons	balance

Table 1.

S-BuOH was dosed into a mixer such that the feed to the column typically contained 330ppm s-BuOH. The calculated feed rate averaged some 4050 g/hr, entering via the center feed point (i.e. tray 20) and the column was operated at a reflux ratio of 2:1, with the column pressure being measured at the base. At a pressure of 1.06bara an average s-BuOH distillate concentration of approximately 20ppm was achieved. When the pressure was reduced to 0.52 bara the concentration of s-BuOH in the distillate reduced to an average of 7ppm

The experiment was then run with a reduced feed supply rate of 3230 g/hr such that the base contained a reduced concentration of s-BuOH (< 5m/m%). The column was operated at between 0.54 and 0.6 bara and under these conditions the distillate no longer contained any detectable s-BuOH (i.e. 1 ppm or less).

### Example 2

#### s-Butanol Esterification and Trans-esterification in the Base of "D7600"

D7600 is a commercial 50 tray distillation column used for the purification of ethyl acetate. A small amount of acetic acid is produced via ethyl acetate hydrolysis and accumulates in the base of the distillation column. It was calculated that, assuming a 17 CuM hydrogenation reactor for converting the MEK to sec-butanol, a measured flow of 21 kgs/hr of acetic acid reaches a steady state concentration of approximately 18 wt% assuming a base purge of 130 kgs/hr. The residence times observed in the base of the column are also dictated by the purge rate and lead to residence times of the order of 60 to 70 hours.

In order to further understand the rates of these processes a test was carried out on the pilot plant where the base composition of the distillation column was adjusted to increase both acid and s-BuOH in the base to 13.34% and 8.85%, respectively.

Table 2 below shows the composition change during the test:

Component	Starting wt%	Wt% after 70 hours	Corrected wt% after 70 hours	Wt% change over 70 hours	Molar change
Acetic Acid	13.34	12.69	10.94	- 2.38	- 0.040
s-BuAc	3.12	10.56	9.12	+ 6.00	+ 0.052
s-Butanol	8.85	5.41	4.67	- 4.18	- 0.056
Et Prop	7.61	8.81	7.61	-	-

Table 2.

Ethyl propionate was expected not to be significantly effected by the reactions taking place and were therefore used as a means for adjusting the compositions for changing sump level.

The results show that the molar increase in s-BuAc is consistent with the decrease in s-Butanol. The data shows that when steady state is reached, using a residence time of 70 hours, 47% of the butanol will have reacted; the remainder will have been purged from the system. In addition the data shows that the loss of acid due to esterification is the predominant reaction accounting for 74% of the butanol reaction. The trans-esterification reaction is slower accounting for 26% of the butanol conversion.

### Example 3

Using the 50 tray pilot plant distillation column referred to in Example 1, a series of tests was carried out using a 2:1 reflux ratio throughout. The results are shown in Table 3 below. Ethyl acetate containing the indicated quantity of sec-butanol impurity was fed to the column at the indicated rate. The concentration of sec-butanol impurity in the ethyl acetate distillate can be seen to fall dramatically to 7 ppm when the column pressure is reduced from 1 bara down to 0.52 bara. Reduction of the feed rate results in a further drop in sec-butanol level in the distillate to less than 1 ppm.

Test No.	Feed Rate	Column Pressure Bara	s-BuOH			Precision
			Feed (ppm)	Base (%)	Distillate (ppm)	
1	3.8	1.0	30	2.3	5	2
2	3.8	1.0	320	4.5	15	3
3	3.8	1.0	320	2.5	10	2
4	4.0	1.0	330	8.0	20	2
5	4.0	0.52	330	9.0	7	2
6	4.2	0.54	330	5.0	0	2

Table 3

Claims:

1. A process for separating ethyl acetate from sec-butanol, said process comprising:  
taking a product stream comprising ethyl acetate and sec-butanol,  
feeding the product stream to a distillation column,  
operating the distillation column at a pressure of less than 1 bar absolute to give an  
ethyl acetate stream and a sec-butanol stream.
2. A process for separating sec-butanol impurity from ethyl acetate, said process  
comprising:  
feeding to a distillation column a product stream comprising at least ethyl acetate  
and sec-butanol,  
operating the distillation column at a pressure of less than 1 bar absolute to  
provide at least  
(1) a stream comprising ethyl acetate as a major component and  
(2) a residue or a second stream which residue or second stream comprises at least  
some sec-butanol from said product stream.
3. A process as claimed in Claim 1 or 2 wherein the pressure in the distillation  
column lies in the range 0.01 and 0.95 bar absolute.
4. A process as claimed in Claim 1 or 2 wherein the pressure in the distillation  
column lies in the range 0.1 and 0.7 bar absolute.
5. A process as claimed in Claim 1 or 2 wherein the pressure in the distillation  
column lies in the range between 0.3 and 0.5 bar absolute.
6. A process as claimed in any one of the preceding Claims wherein the product  
stream is fed to the distillation column between one-quarter and three-quarters of

the way up the column.

7. A process as claimed in any one of the preceding Claims wherein the product stream is fed to the central third of the distillation column.
8. A process as claimed in any one of the preceding Claims wherein the ethyl acetate / sec-butanol stream is derived from a stream (3) comprising ethyl acetate and methyl ethyl ketone (MEK), wherein the MEK has been hydrogenated to produce the sec-butanol.
9. A process as claimed in Claim 8 wherein the ethyl acetate / MEK stream (3) has itself been derived from the reaction of ethylene and acetic acid, or from the conversion of an alcohol feedstock to ethyl acetate by i) dehydrogenation, ii) oxidation, iii) reaction with an aldehyde or iv) oxidation to the corresponding aldehyde followed by the Tischenko reaction.
10. A process as claimed in Claim 8 or 9 wherein the MEK in the product stream (3) is hydrogenated to produce sec-butanol by contacting all or a part of product stream (3) with hydrogen in the presence of a selective hydrogenation catalyst.
11. A process as claimed in Claim 9 wherein the selective hydrogenation catalyst comprises a 3-5wt% Ru catalyst supported on carbon or silica.
12. A process for purifying ethyl acetate substantially as hereinbefore described in the Examples.
13. Ethyl acetate prepared by the process described in any one of the preceding claims.

## INTERNATIONAL SEARCH REPORT

International Application No.

PCT/GB 02/03411

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C07C67/54 C07C69/14 C07C29/80

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C07C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ, COMPENDEX, INSPEC

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 990 638 A (KVAERNER PROCESS TECH LTD) 5 April 2000 (2000-04-05) paragraphs '0050!', '0057!'-'0061!', '0077!', '0079!; claims 1,7-14; example 13; tables 1-3	1-11, 13

☐ Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

## \* Special categories of cited documents:

- 'A' document defining the general state of the art which is not considered to be of particular relevance
- 'E' earlier document but published on or after the international filing date
- 'L' document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- 'O' document referring to an oral disclosure, use, exhibition or other means
- 'P' document published prior to the international filing date but later than the priority date claimed

'T' later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

'X' document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

'Y' document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

'&' document member of the same patent family

Date of the actual completion of the international search

8 October 2002

Date of mailing of the international search report

12/11/2002

Name and mailing address of the ISA

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Authorized officer

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# INTERNATIONAL SEARCH REPORT

International application No.  
PCT/GB 02/03411

## Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:  
because they relate to subject matter not required to be searched by this Authority, namely:
  
2. ☒ Claims Nos.: 12  
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:  
see FURTHER INFORMATION sheet PCT/ISA/210
  
3. ☐ Claims Nos.:  
because they are dependant claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

## Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this International application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.
  
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
  
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:
  
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.
- ☐ No protest accompanied the payment of additional search fees.

# INTERNATIONAL SEARCH REPORT

International Application No. PCT/GB 02 03411

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

Continuation of Box I.2

Claims Nos.: 12

Claim 12 relies on the examples of the description. Such a formulation is absolutely unclear and does not fulfill the requirements of Rule 6.2a) and 6.3 PCT. It has accordingly not been searched.

The applicant's attention is drawn to the fact that claims, or parts of claims, relating to inventions in respect of which no international search report has been established need not be the subject of an international preliminary examination (Rule 66.1(e) PCT). The applicant is advised that the EPO policy when acting as an International Preliminary Examining Authority is normally not to carry out a preliminary examination on matter which has not been searched. This is the case irrespective of whether or not the claims are amended following receipt of the search report or during any Chapter II procedure.

**INTERNATIONAL SEARCH REPORT**  
Information on patent family members

International Application No

PCT/GB 02/03411

Patent document cited in search report	Publication date	Patent family member(s)	Publication date	
EP 0990638	A	05-04-2000	EP 0990638 A1	05-04-2000
			AU 6107399 A	26-04-2000
			BR 9914249 A	19-06-2001
			EP 1117631 A1	25-07-2001
			GB 2357504 A	27-06-2001
			WO 0020375 A1	13-04-2000
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